

The model for thermodynamic description of metalloid solution processes in molten metals and oxide – sulfide melts

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Abstract. The methods and the programs for computer analysis of fundamental characteristics of metallurgic systems and processes, in particular, the chemical equilibrium calculation methods, including the evaluation of equilibrium constant and equilibrium system composition are developed. Metalloid dissolving in liquid metals, binary molten metals, and sulfide and oxide-sulfide melts is simulated. The paper contains calculation of contributions of various states into entropy S of liquid metal systems containing ions of copper, iron, nickel, cobalt, titanium, manganese, aluminum, etc on dissolving oxygen and sulphur in the systems. The effectiveness factors of metalloid, oxides and FeS in oxide-sulfide melts are analyzed. The paper shows application of the polymer model equations to calculation of thermodynamic characteristics of interphase distribution of oxygen and sulphur between liquid metal and oxide-sulfide melts.

The calculations of equilibrium in high-temperature multiphase, multicomponent systems are quite a challenge since they require sets of theoretical and experimental data on physical and chemical properties of the agents involved in the process.

High-temperature processes with liquid phases involved are multiple-stage and characterized with motion and redistribution in parallel of a large number of elementary particles, and are connected with changes in electron density and nature of interparticle interaction in melts.

We have developed the methods and programs for computer analysis of fundamental thermodynamic characteristics in high-temperature processes accompanying interconversion of solid and gas phases, and processes involving metal, sulfide and oxide-sulfide melts. The paper demonstrates the methods for calculation of chemical equilibrium, including the evaluation of the equilibrium constant and the equilibrium system composition within a wide range of temperatures and pressures.

The computer analysis is conducted with regard to concentration dependences of entropies S and excess entropies ΔS of mixing, activity coefficients f_x of metalloid, namely, of oxygen and sulphur based on model principles [1-4] for a number of pure metals and binary copper-, iron-, nickel-, titanium-base melts (55 systems in all) close to melting points. In addition, the study determines the parameters of the first and second orders of interparticle interactions in molten metals containing metalloid atoms was performed.

Analysis of the known models has shown that they all are based on assumptions of random distribution of atoms in metal melts and do not consider the system entropy change which always occurs when dissolving different elements in liquid.

We have developed the model of dissolving metalloid atoms in molten metal which takes into account the parameters characterizing nonadditivity of binding energy of different pairs of atoms in liquid and their ordered arrangement to a certain extent at the temperatures that do not too exceed the alloy melting point. These parameters are ΔH_{dissol} and ΔS_{dissol} , i.e. change in the melt enthalpy and entropy when dissolving a metalloid atom in the melt.

ΔH_{dissol} is calculated based on the formula of $\Delta H_{\text{dissol}} = (\Delta H_{x[A]} + \Delta H_{x[B]} - \Delta H_{[A+B]})$, where $\Delta H_{x[A]}$ and $\Delta H_{x[B]}$ are thermal effects typical for reaction of dissolving metalloid atoms in pure liquid metals; $\Delta H_{[A+B]}$ is enthalpy change caused by formation of binary metal melt, and depending on concentration; $\Delta H_{x[A]}$, $\Delta H_{x[B]}$, $\Delta H_{[A+B]}$ are taken from [5-8] for the systems under study.

ΔS_{dissol} is also presented as the difference between the additive entropy of the alloy components interacting with metalloid atoms and the entropy of mixing of metal atoms forming binary alloy without metalloid atoms. The change in the entropy of the metal system containing dissolved metalloid atoms as a function of the composition is calculated using the data [9,10] of X-ray structural analysis of the respective metal melts.

It is determined that energy unsimilarity of atom interaction and the tendency to microordering between particles of different elements is mostly typical for the melts of copper-manganese-oxygen and copper-manganese-sulphur systems within the whole range of compositions. The liquid metal systems of copper-silver, copper-aluminium, barium-magnesium, lead-tin, lead-bismuth and tin-bismuth are characterized by local areas of ordering of atoms of the same elements at mean and high concentrations of the second component with the metalloid presence.

The calculations demonstrate that the coefficients of sulphur activity are more than those of oxygen. This fact proves the assumptions [5,6,11] with regard to oxygen behavior in melts as an element of higher electronegativity and less ion sizes.

It is determined that as the concentration of the second metal component of an alloy is increasing, the oxygen activity coefficient f_O is decreasing. At that the most significant reduction of f_O is observed in the systems of titanium-zirconium, titanium-vanadium, titanium-aluminum. This process can arise from material difference between the energies of interparticle interactions E_{ij} in melts. The oxygen activity coefficients in binary titanium-base melts can be arranged in a row: $f_O^{\text{AL}} < f_O^{\text{V}} < f_O^{\text{Zr}} ; f_O^{\text{Mo}} < f_O^{\text{Cu}} < f_O^{\text{Ni}}$. This sequence qualitatively correlates with the values characterizing the change in standard Gibbs energies ΔG^0 for formation of oxides of the respective elements.

The principles [12-15] of the polymer model for liquid oxide systems are the basis for developing the program of calculation of activities and parameters of equilibrium distribution of elements between metal and multicomponent oxide-sulfide melt.

The activity a_i of oxides is calculated [14] considering the melt polymerization constant, K_P :

$$\ln K_P = N_{\text{SiO}_2} N_{\text{Me}'\text{O}} / (S_1 S_2) \ln K_{P, \text{Me}'\text{O} - \text{SiO}_2} + N_{\text{Al}_2 \text{O}_3} N_{\text{Me}'\text{O}} / (S_1 S_2) \ln K_{P, \text{Me}'\text{O} - \text{Al}_2 \text{O}_3} + \\ + N_{\text{SiO}_2} N_{\text{Me}''\text{O}} / (S_1 S_2) \ln K_{P, \text{Me}''\text{O} - \text{SiO}_2} + N_{\text{Al}_2 \text{O}_3} N_{\text{Me}''\text{O}} / (S_1 S_2) \ln K_{P, \text{Me}''\text{O} - \text{Al}_2 \text{O}_3} + \\ + N_{\text{SiO}_2} N_{\text{Me}''' \text{O}} / (S_1 S_2) \ln K_{P, \text{Me}''' \text{O} - \text{SiO}_2} + N_{\text{Al}_2 \text{O}_3} N_{\text{Me}''' \text{O}} / (S_1 S_2) \ln K_{P, \text{Me}''' \text{O} - \text{Al}_2 \text{O}_3} ; \quad (1)$$

$$\ln a_{\text{SiO}_2} = \ln(K_P^2 (N_m N_{\text{SiO}_2} / N_O^2 S_1)) + N_{\text{Al}_2 \text{O}_3} (1-\alpha) / (1-N_{\text{SiO}_2} - N_{\text{Al}_2 \text{O}_3}) S_1 \times \\ \times \sum N_m \ln (K_{P, m-\text{SiO}_2} / K_{P, m-\text{Al}_2 \text{O}_3}); \quad (2)$$

$$\ln a_{\text{Al}_2 \text{O}_3} = \ln(K_P^2 (N_m N_{\text{Al}_2 \text{O}_3} / N_O^2 S_1)) + N_{\text{SiO}_2} (1-\alpha) / (1-N_{\text{SiO}_2} - N_{\text{Al}_2 \text{O}_3}) S_1 \times \\ \times \sum N_m \ln (K_{P, m-\text{Al}_2 \text{O}_3} / K_{P, m-\text{SiO}_2}); \quad (3)$$

$$\ln a_i = \ln(N_O^2 N_{\text{Me}}^{(+)} + (1-\alpha) / (1-N_{\text{SiO}_2} - N_{\text{Al}_2 \text{O}_3})^2 \times \\ \times \sum N_m \ln (K_{P, i-\text{SiO}_2} / K_{P, m-\text{SiO}_2})^{N_{\text{SiO}_2}} (K_{P, i-\text{Al}_2 \text{O}_3} / K_{P, m-\text{Al}_2 \text{O}_3})^{N_{\text{Al}_2 \text{O}_3}}). \quad (4)$$

where $S_1 = N_{\text{SiO}_2} + N_{\text{Al}_2\text{O}_3}$, $S_2 = N_{\text{Me}^+\text{O}} + N_{\text{Me}^{2+}\text{O}} + N_{\text{Me}^{3+}\text{O}}$; $N_{\text{O}^{2-}}$ is the concentration of free oxygen ions, $N_{\text{O}^{2-}} = (1-3N_{\text{SiO}_2} + 2\alpha N_{\text{SiO}_2}) / (1-2N_{\text{SiO}_2} + \alpha N_{\text{SiO}_2})$; $N_{\text{Me}^{(+)}}$ is the concentration of metal cations; α is the degree of melt polymerization; N_m is the mole fraction of basic oxide in molten aluminosilicate containing K of basic oxides; K_p is the melt polymerization constants; values of K_p are given in [14,15].

In order to calculate oxygen equilibrium content [O] in metal, L_O , i.e. coefficient of oxygen distribution between liquid metal and oxide melt, the following equation is used:

$$L_O = a_{\text{FeO}} / a_{[\text{O}]} = a_{\text{FeO}} / f_{[\text{O}]} [\text{O}]. \quad (5)$$

where $f_{[\text{O}]}$, i.e. oxygen activity coefficient in liquid metal is determined in [16] taking into account parameters e^{I} of oxygen interaction with dissolved elements.

Coefficient α_o can be calculated according to the empirical equation [17]:

$$\lg L_O = 6320 / T - 2.734. \quad (6)$$

The constant of desulfurization equilibrium

$$K_S = N_{(\text{S}^{2-})} [\text{O}] / (N_{(\text{O}^{2-})} [\text{S}]). \quad (7)$$

This formula includes the free sulphur concentration, i.e. $N_{(\text{S}^{2-})} = ((\% \text{S}) / M_S) / \Sigma n^-$; Σn^- means the total number of anions in the melt, including the number of ions-complexing agents which is calculated based on the polymer model equations; M_S is the molecular weight of sulphur.

The temperature dependence K_S is described in the equation [15]:

$$\ln K_S = -17000/T + 5.46. \quad (8)$$

In case of high concentrations of acidified oxides in oxide melts

$$K_S = (a_{(\text{Fe}^{2+})} a_{(\text{S}^{2-})} / [\text{S}]) = a_{(\text{FeS})} / [\text{S}], \quad (9)$$

where $a_{(\text{FeS})}$ is FeS activity in oxide melt; $a_{(\text{FeS})} = N_{(\text{Fe}^{2+})} N_{(\text{S}^{2-})}$.

According to [16] for the case under review

$$\lg K_S = -3160/T + 0.46. \quad (10)$$

Sulfide capacity C_S is connected with K_S [16]:

$$\lg C_S = \ln K_S + \ln a_{(\text{O}^{2-})}, \quad (11)$$

where $a_{(\text{O}^{2-})}$ is the activity of oxygen ions in oxide melt corresponding to its mole fraction $N_{(\text{O}^{2-})}$.

Table 1. Compositions of Molten Oxide-Sulfides under Study

No.	Composition, Number of Moles per 100 g of Melt				
	CaO	MgO	FeO	SiO ₂	(S)
1	0.178	0.150	1.120	0.020	0.0025
2	0.536	0.125	0.815	0.085	0.0060
3	0.102	0.082	1.236	0.017	0.0028
4	0.716	0.126	0.656	0.120	0.0081
5	0.711	0.108	0.655	0.114	0.0047
6	0.310	0.077	1.042	0.035	0.0028
7	0.276	0.108	1.046	0.059	0.0037
8	0.580	0.98	0.817	0.046	0.0119
9	0.304	0.068	1.050	0.046	0.0041
10	0.610	0.145	0.753	0.091	0.0069
11	0.690	0.191	0.463	0.326	0.0016
12	0.680	0.219	0.348	0.455	0.0016
13	0.287	0.242	0.845	0.194	0.0031
14	0.370	0.244	0.671	0.306	0.0025
15	0.541	0.327	0.393	0.463	0.0016
16	0.333	0.163	0.870	0.187	0.0022
17	0.576	0.172	0.525	0.372	0.0041

The study includes computer analysis of activities a_i of components for fifty-five oxide-sulfide melts of the system $\text{CaO} - \text{MgO} - \text{MnO} - \text{FeO} - \text{SiO}_2 - \text{Al}_2\text{O}_3 - \text{MeS}$ within the temperature from 1823 to 2073 K. Sulfide capacities and coefficients of oxygen and sulphur distribution between liquid metal and oxide-sulfide melt are calculated, and the equilibrium concentrations of elements in metal matrix are determined.

As an example, Table 1 and Table 2 show the compositions of some oxide-sulfide melts under study and the above mentioned characteristics are calculated in specially developed program.

Table 2. Activity of Oxide-Sulfide Melt Components and Equilibrium Concentrations of Oxygen and Sulphur in Metal Matrix at 1873K

No.	a_{CaO}	a_{MgO}	a_{FeO}	a_{FeS}	[O]	[S]	Cs	Cs/76/	[O]	[S]	Cs
									According to [18]		
1	0.1133	0.9936	0.7753	0.0058	0.1995	0.0228	0.0584	0.0015	0.240	0.021	0.0585
2	0.2735	1.0568	0.6054	0.0230	0.1384	0.0328	0.0557	0.0062	0.119	0.031	0.0557
3	0.0659	0.9882	0.8671	0.0018	0.1986	0.0246	0.0586	0.0010	0.216	0.023	0.0586
4	0.03383	1.1462	0.5272	0.0026	0.1107	0.0340	0.0541	0.0116	0.097	0.030	0.0541
5	0.3528	1.1412	0.5253	0.0015	0.1202	0.0200	0.0543	0.0122	0.116	0.017	0.0544
6	0.1882	0.9984	0.7392	0.0015	0.1692	0.0220	0.0578	0.0027	0.151	0.020	0.0578
7	0.1496	0.9937	0.7473	0.0024	0.1711	0.0310	0.0567	0.0020	0.171	0.028	0.0568
8	0.3355	1.0335	0.5752	0.0047	0.1117	0.0490	0.0574	0.0096	0.094	0.042	0.0574
9	0.1774	0.9966	0.7504	0.0024	0.1572	0.0230	0.0573	0.0025	0.133	0.019	0.0573
10	0.3072	1.0805	0.5584	0.0022	0.1007	0.0370	0.0555	0.0083	0.082	0.030	0.0555
11	0.1881	1.6784	0.5912	0.0006	0.1253	0.0190	0.0405	0.0036	0.119	0.020	0.0406
12	0.1078	2.4341	0.5482	0.0006	0.1154	0.0370	0.0262	0.0019	0.110	0.034	0.0264
13	0.0954	1.0471	0.6804	0.0016	0.1777	0.0370	0.0498	0.0011	0.222	0.044	0.0498
14	0.08325	1.2272	0.6582	0.0017	0.2005	0.0480	0.0415	0.0009	0.230	0.051	0.0416
15	0.07281	2.0799	0.5222	0.0007	0.1958	0.0510	0.0265	0.0010	0.174	0.049	0.0265
16	0.1141	1.0479	0.7043	0.0008	0.1613	0.0200	0.0501	0.0014	0.194	0.022	0.0501
17	0.1153	1.6446	0.6541	0.0015	0.1428	0.066	0.0353	0.0017	0.138	0.076	0.0357

The obtained results allow predicting the refining capability of the studied liquid oxide systems.

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